EFFECT OF REDUCING AGENTS TYPES - ON THE SYNTHESIS OF SILVER NANOPARTICLES

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ABSTRACT

In recent years, metal nanoparticles such as silver have been studied extensively due to their unique properties that are significantly different from those of bulk material. In this study, silver nanoparticles were synthesized by chemical reduction method with different type and concentration of reducing agents which is glucose and Cetyl trimethylammonium bromide (CTAB). The effect of the reducing agent on the size and morphology of the silver nanoparticles has been investigated. In this study, the formation and morphology of nanosized silver nanoparticles has been characterized by using UV-VIS spectroscopy, and Field Emission Scanning Electron Microscopy analysis (FESEM), respectively. Meanwhile, the purity of element on the synthesized silver nanoparticles has been carried out by Energy-dispersive X-ray spectroscopy (EDX). From the results of UV-Vis, silver nanoparticles that used glucose as a reducing agent showed narrow size distribution compared to CTAB. The maximum absorbance of silver nanoparticles for glucose as reducing agent is 0.481 while for CTAB is 0.831. The average size of the resulting silver nanoparticles for the concentration were determined by Image J software and result for the size is 10 nm with the high purity (91.95 % weight) using glucose and (77.78 % weight) when used CTAB as a reducing agents. During sample preparation, glucose showed a slow reaction as reducing agents compare with CTAB, which is more suitable to control a size and morphology of silver nanoparticles. The synthesis of silver nanoparticles has remains a formidable challenge in order to find a simple way to generate monodisperse silver nanoparticles with small size at high concentration.

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ABSTRAK

Dalam tahun-tahun kebelakangan ini, nanopartikel logam seperti perak telah dikaji secara meluas kerana sifat-sifat unik yang ketara berbeza daripada bahan pukal. Dalam kajian ini, nanopartikel perak telah disintesis melalui kaedah pengurangan kimia dengan jenis yang berbeza dan kepekatan agen penurunan yang glukosa dan cetyl trimethylammonium bromida (CTAB). Kesan agen penurunan kepada saiz dan morfologi nanopartikel perak telah disiasat. Dalam kajian ini, pembentukan dan morfologi nanopartikel perak nanosized telah disifatkan dengan menggunakan UV-VIS spektroskopi, dan analisis Field Pelepasan Imbasan Elektron Mikroskop (FESEM), masing-masing. Sementara itu, berhadas elemen pada nanopartikel perak disintesis telah dijalankan oleh Tenaga serakan X -ray spektroskopi (EDX). Daripada keputusan UV- Vis, nanopartikel perak yang digunakan glukosa sebagai agen penurunan menunjukkan taburan saiz sempit berbanding CTAB. Absorbans optimum nanopartikel perak untuk glukosa sebagai agen penurunan adalah 0,481 dan bagi CTAB mengurangkan ejen adalah 0.831. Saiz purata nanopartikel perak yang terhasil untuk kepekatan ditentukan oleh Imej perisian J dan menyebabkan untuk saiz ialah 10 nm dengan keaslian yang tinggi (91.95 % berat) menggunakan glukosa dan (7.78 % berat) apabila menggunakan CTAB sebagai agen penurunan . Semasa penyediaan sampel, glukosa menunjukkan reaksi yang perlahan mengurangkan ejen membandingkan dengan CTAB, yang lebih sesuai untuk mengawal saiz dan morfologi nanopartikel perak. Sintesis nanopartikel perak telah kekal sebagai cabaran yang besar untuk mencari cara yang mudah untuk menjana nanopartikel perak monodisperse dengan saiz kecil pada kepekatan yang tinggi.

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LIST OF ABBREVIATIONS

^{o}C	Degree Celsius
%	Percentage
ml	Mililiter
O	Oxygen
C	Carbon
Cl	Chlorine
nm	nanometer
mM	mili Molar
keV	Kilo electron Volt
AA	Ascorbic Acid
kHz	Kilohertz
g	Gram
Ag	Silver
$AgNO_3$	Silver Nitrate
Q	Amount of Material
AgNPs	Silver Nanoparticles
SPR	Spectrum Plasmon Resonance
CTAB	Cetyl Trimethylammonium Bromide
UV-Vis	Ultraviolet Visible
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
ANOVA	Analysis of Variance

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF RESEARCH

Nanomaterial is one of essential building in nanotechnology field that emerge from physical, chemical and engineering sciences with the techniques and procedures materials at nanoscale level (Mahendran et al., 2013). The historical development of nanoparticles starting with Paul Ehrlich and then first attempts by Ursula Scheffel and colleagues in the late 1960s and early 1970s which described from a personal point of view (Kreute, 2006). In general, nanoparticles are defined as particulate dispersions or solid particles with a size in the range of 10 to 100 nm (Sally et al., 2007). It is accepted in the context of nanoscience and nanotechnologies, the units should only be those of dimensions, rather than of any other unit of scientific measurement (Kholoud et al., 2009). The scientific interest of nanoparticles is depends on the effectively a bridge between bulks materials and atomic or molecular structures regarding to its size at nanoscale and observations of size dependent properties (Kandarp & Mihir, 2013).

The characteristic of silver nanoparticles has a unique electronic, optical, thermal and catalytic property. The nanometer-size particles show unique because it can considerably change physical, chemical and biological properties compare to the macro scaled counterparts, due to their high surface to volume ratio. While the optical characteristic of nanoparticles which is including transparency, absorption, luminescence and scattering is depended on their particle size as it will determined their surface properties (Christina et al., 2011). The characteristic of silver nanoparticles can be obtained by analyzing the spectral properties at absorbing and scattering of light. The silver nanoparticles will delocalized and shared amongst neighbouring particles when the particles are aggregate and the conduction electrons are near between the each particles surface (Kandarp & Mihir, 2013).

Moreover, the high electrical conductivity, stability and the low sintering temperature usually included in conductive inks, pastes and filler. Additional applications include molecular diagnostics and photonic devices also show the advantages of the optical properties of the silver nanoparticles. However, in spite of these advantages, nanoparticles do have limitations. For example, their small size and large surface area can lead to particle aggregation, which making physical handling of nanoparticles difficult in liquid and dry forms. Different parameters such as time, temperature and the concentration of the reducing agent and the surfactant can be manipulated in order to control the particles size distribution (Mohanraj & Chen, 2006). In all synthesis method, it is vital to obtain uniform, narrow particles distribution as well as low particles agglomeration.

Furthermore, silver nanoparticle is also commonly used as antibacterial application such as wound dressing, medical catheters, and bone prostheses (Sahoo et al., 2009). In the treatment of wounds, silver nanoparticles can be replaced with the silver sulfadiazine as an effective agent (Kandarp & Mihir, 2013). Recently, many new industries involves in production of antibacterial gels using silver nanoparticles. Nanoparticles also play a crucial role in inhibiting bacterial growth in aqueous such as in water treatment because of it high reactivity due to the large surface to volume ratio. It also contains material that can be used in water treatment. The reduction of silver ions to silver metals can be observed as silver nanoparticles display intense colour due to surface Plasmon resonance which were depending on the size of the particles. It has been discovered by previous work (Maribel et al., 2009) that at room temperature, the reaction would take several weeks to reach completion but at reflux the reaction would be finished within seconds. At the higher temperatures, the particles become more disperse and the nanoparticles also were formed at room. The dispersions of silver nanoparticles display intense colors due to the plasmon resonance absorption (Maribel et al., 2009).

Furthermore, silver nanoparticles also can use as a conductive applications for the conductive inks to enhance thermal and electric conductivity. This product bringing a changing in the electrical technology field. Besides that, silver nanoparticles also has been used in home application such as for washing machine, refrigerator and aqua guards (Felba., 2011). In this study, the reduction of silver nanoparticles will be carried out by organic and inorganic reducing agents. Glucose and cetyl trimethylammonium bromide (CTAB) will be used as reducing agent while ascorbic acid as a surfactant to control the dispersion of silver nanoparticles. It is very important to stabilize dispersive nanoparticles during the course of silver nanoparticle preparation, and protect the nanoparticles that can be absorbed on or bind onto nanoparticle surface.

1.2 PROBLEM STATEMENT

The synthesis of silver nanoparticles also is one of the challenging processes because the most important in this synthesis is to get narrow size distribution which has a range from 10 to 100 nm. This study only focused on the effect of reducing agent concentration on the size and morphology of silver nanoparticles. The challenge in synthesis of silver nanoparticles is to find a simple way to generate monodisperse silver nanoparticles. To achieve the narrow size distribution, the parameter such as of concentration should be controlled using chemical reduction method. Therefore, the method of synthesize silver nanoparticles remains a formidable challenge in order to find a simple way to generate monodisperse silver nanoparticles (Jiping et al., 2011). To keep the size of nanoparticles small, the initial concentration of silver salt in a reaction system must be lower and the reducing agents should be strong. If the initial concentration is high, then silver particles may grow too large. This study only focused on the effect of reducing agent concentration on the size and morphology of silver nanoparticles.

The other challenging in synthesis of silver nanoparticles is due to the difficulty to control the stability of the size and shape of particles in aqueous solution for the long term (Amadeus et al., 2012). It is depends on the medium of silver nanoparticles are immersed in because when the nanoparticles are applied and stored in aqueous condition, the silver nanoparticles will interact with biological matter and living cells and will affected to the aggregation, size and shape of the nanoparticles and long-term stability (aging). In view of the rapidly progress, silver nanoparticles is growing need in the different fields for many applications.

The technological and environmental also is one of challenges where in the areas of solar energy conversion, catalysis, medicine and waste treatment also consider in order to control the size particles and composition of silver nanoparticles (Rupiasih et al., 2013). In addition, the silver nanoparticles have unique catalytic, optical, electrical and antimicrobial properties. Silver is a nontoxic inorganic antimicrobial agent, which is inhibiting the microbe's growth. So, by using the concentration of reducing agents in synthesis silver nanoparticles can control the size and shape distribution in long term.

1.3 OBJECTIVE

The main objective of this research is to study the optimum concentration of reducing agent on the synthesis of silver nanoparticles by determine:

a) Effect of concentration of glucose as a reducing agent.
b) Effect of concentration of Cetyl trimethylammonium bromide (CTAB) as a reducing agent

1.4 SCOPE OF RESEARCH

In synthesis of silver nanoparticles, the main scope of this study is to determine the optimum concentration of reducing agents with the narrow size distribution which has a range from 10 to 100 nm. The chemical reduction method will be used to synthesize the silver nanoparticles because it is the most commonly methods used, simplest, and easiest. Glucose and cetyl trimethylammonium bromide (CTAB) will be used as a reducing agent with difference concentration, while ascorbic acid as a surfactant.

In order to get the results, UV-Vis absorption spectroscopy is used to monitor the formation of the silver nanoparticles and the change color of solution also can illustrate from visible observation. The optimum absorbance for the sample can showed the optimum concentration for the sample. Therefore, the Field emission scanning electron microscopy *(*FESEM*)* will be used to get the structural properties of silver nanoparticles with high-resolution surface images and image J software is used in order to determine the particles size distribution, where the size distribution can illustrated from the shape of histogram. After that, the elemental analysis of sample also has been performed using energy dispersion X-ray analysis (EDX). This analysis also to detect the other impurity contains in the sample except the pure silver, with no oxide.

1.5 RATIONAL AND SIGNIFICANCE OF RESEARCH

Silver nanoparticles such as silver have been studied extensively due to their unique properties that are significantly different from those of bulk material. These unique properties could be attributed to their small size and large surface area which is in many applications including electronic, catalyst and photonic. Currently, nanoparticles based on silver nanoparticles are applied in antimicrobial coatings, and many textiles, keyboards, wound dressings, biomedical devices, ink-jets, inks, safety labels, pigments, conducting strips. Based on this research, the variable parameter is the concentration of glucose and CTAB as reducing agents. Each different concentration of reducing agents will give the different result of morphology and the size of distribution. The narrow size distribution will produce from the difference concentration of glucose and CTAB, which the results from UV-Vis spectroscopy for the different trends of graph. When the wavelengths for the concentration of reducing agents increase, the size of particles also increase. After that, the increasing concentrations of reducing agent, the color of the solution will changes. According this study, the selected for the best result is depending on the uniform shape and narrow size distribution with determine the optimum concentration reducing agents.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

A reducing agent is the element or compound in a reduction oxidation reaction that donates an electron to another (John, 2003). The surfactants are to control the morphology and particles size of silver nanoparticles. If the surfactant molecule is dissolved in a nonpolar medium, it can intersect with other part from the nonpolar dispersant (Palash et al., 2010). The important role of this process is the value of pH, temperature, stabilizer and concentration. From the previous study (Sahoo et al., 2009), the optimum pH is found between 8.5 – 9.0 as it a uniform particles size and narrow distribution. Meanwhile, when the value of pH is higher, the silver nanoparticles are more stable.

During synthesis process, the stabilizer adsorbs on the solid-liquid interface and forms a layer of molecular. It also can reduce surface tension by reducing the absorption capability. Therefore, when the concentration of reducing agent is increase, the solutions become more cluster but it does not affect the particles size distribution. Besides that, it also reported that the reduction process of silver ions is higher in alkaline solution (Manjeet et al., 2009). Furthermore, the large amount of the stabilizer also can prevent nanoparticles reactions from the other compound. It is also become more entanglement in the dense network of the stabilizer (Malina et al., 2012).

According the previous study (Chang et al., 2009), the chemical reduction method is used for reduction of $AgNO_3$ by sodium borohydride ($NaBH_4$) as a reducing agent and sodium dodecyl sulfate (SDS) as a surfactants. From previous work, it shows that when the concentration of AgNO3 increased, the color of solution changed from yellow to brown. Meanwhile, a weak absorption maximum of surface Plasmon peaks was observed at 400 nm, indicating the formation of silver nanoparticles. The intensity of the maximum Plasmon peak was reported to be increased as concentration of AgNO3 increase, indicating that more silver nanoparticles were formed.

2.2 SILVER NANOPARTICLES

Shape and size control of silver nanoparticles is a promising strategy to tailor their physical and chemical properties for various applications in the field of photonics, catalysis, medical research and surface enhanced Raman spectroscopy (SERS). Superior physical and chemical properties were observed for the metal nanostructures with complex shapes (Etacheri et al,. 2010). A typical example is the shape and size dependent optical properties exhibited by triangular silver nanoplates. Triangular plates show three surface plasmon resonance (SPR) bands corresponding to dipole and quadruple plasmon resonance, but only one SPR band is observed for spherical silver nanoparticles. A large number of aqueous and non-aqueous methods were reported in the past decade for the synthesis of silver nanoparticles having different size and shapes such as rods, prisms, cubes, wires and disks (Etacheri et al,. 2010).

Colloidal silver nanoparticles synthesized in a polymer matrix have wide applications as biosensors, antimicrobial agents, catalysts and in new generation light weight electronic devices. A battery of techniques is available in the literature to synthesize silver nanoparticles in aqueous as well as in non aqueous medium. The general philosophy of the synthesis of metal nanoparticles from its salt solution is based on using a reducing agent in presence of a capping agent. Capping agents keep the nanoparticles away from agglomeration besides modifying their morphology as well (Patakfalvi1 et al., 2006).

2.3 OPTICAL PROPERTIES OF SILVER NANOPARTICLES

UV-VIS absorption spectra have been proved to be quite sensitive to the formation of silver colloids because silver nanoparticles exhibit an intense absorption peak due to the surface Plasmon excitation. The absorption band in visible light region (350 nm – 550 nm, Plasmon peak at 445 nm) is typical for silver nanoparticles. The Plasmon peak and the full-width of half-maximum (FWHM) depend on the extent of colloid aggregation. To monitor stability of the silver nanoparticles, we have measured the absorption of the nanoparticles after different periods of time (Sally et al., 2007). In this research, the stability of particles size distribution has determined by different concentration of reducing agents.

There was no obvious change in peak position, except for the increase of absorbance. As the particles increase in size, the absorption peak usually shifts toward the red wavelengths. Increase of absorption indicates that amount of silver nanoparticles increases. The stable position of absorbance peak indicates that new particles do not aggregate. One can understand that since the silver colloidal particles possessed a negative charge due to the adsorbed citrate ions, a repulsive force worked along particles and prevented aggregation (Sally et al., 2007).

To determine the particle size we performed several calculations changing the radius of particles and compared absorption dependencies on wavelength with the experimental UV-Vis absorption spectrometry results. In theoretical calculations the radius of particle was changed from 5 nm to 100 nm. We have chosen scattering from many spheres, because there was possibility that particles in colloidal solution are not uniform (Sally et al., 2007).

2.4 REDUCING AGENTS

The reduction of silver cations at different reducing agent/loading agent molar ratios, when the reducing agent is increased in the same mixture of $AgNO3$. The maximum absorption band is shifted to shorter wavelengths. UV–vis absorption bands when the reducing agent concentration is increased, an increase of the reducing agent will produces an absorption band shift to shorter wavelengths. The position of the maximum absorption bands shifted to shorter wavelengths when concentration was increased, and the resulting colors are formed in a different order (from violet to orange) during the synthesis process.

However, when the molar was increased, the maximum absorption band shifted to short wavelengths with a corresponding change of color (brown or green). Furthermore, when higher molar was added to the solution (with orange color only), a new intense absorption band appeared at 100 nm which was indicative of the formation of nanoparticles with spherical shape. These same spectral absorption variations in both regions have been observed with higher concentrations (Perdo et al., 2013).

2.5 STABILITY

Stability of the silver nanoparticle formed in a solution is a highly challenging area when considering the size and shape dependant properties. The shape of silver nanoparticles undergo etching and finally convert to spherical particles resulting in a blue shift of the in-plane dipole resonance. The large blue shift, which can be up to 100 nm in magnitude, is a direct measure of particle instability and a small blue shift value usually indicates higher particle stability. An etching study of the green sol up to 1 hr after the final addition of $Ag+$ has been performed to examine the stability of the formed nanoparticles. In the present case, the blue shift observed for triangular nanoparticles were very small (5 nm), which clearly indicate the formation of stable silver nanoparticles (Vinodkumar et al., 2010).

2.6 GROWTH OF SILVER NANOPARTICLES

Growth of the nanoparticles was controlled by only varying the concentration such as ascorbic acid. A single Plasmon resonance around 400 nm was formed without ascorbic acid which indicates the presence of only spherical nanoparticles (18 nm size). Crystallization of triangular nanoparticles and a corresponding second Plasmon resonance at a higher wavelength were observed as a result of increasing the amount of ascorbic acid. A gradual red shift of second Plasmon resonances were also observed on increasing the concentration of ascorbic acid and a green coloured sol containing biggest particles were obtained using 50 mM ascorbic acid. Absorption band associated with spherical nanoparticles was also found in all other nanoparticles colloids. Intensity ratios of these peaks were found to be highly dependent on the concentration of ascorbic acid. The red coloured sol containing 10 mM ascorbic acid was found to have a higher intensity peak around 400 nm and a lower one around 500 nm (Vinodkumar et al., 2010).

On increasing the ascorbic acid concentration, the lower wavelength peak intensity decreases with a corresponding intensity increase of the higher wavelength peak. Shifting of the plasmon resonances to higher wavelength associated with a decrease in absorption intensity of spherical particles indicates the growth of triangular silver nanoparticles on the expense of spherical nanoparticles. Thus spherical and triangular nanoparticles were found to be stabilized at lower and higher ascorbic acid concentrations respectively. From these results it is clear that the concentration of ascorbic acid play an important role in the growth of triangular silver nanoparticles (Vinodkumar et al., 2010).

2.7 CHEMICAL REDUCTION METHOD

In 1857, Micheal Faraday, for the first time reported a systematic study of the synthesis colors of colloidal gold using chemical reduction route (Asim et al., 2012). The chemical reduction method is one of the commonest methods to synthesize of silver nanoparticles because of its convenient operation, ease of control and simple. The chemical reduction method involves the reduction of $AgNO_3$ by a reducing agent in the presence of a suitable stabilizer, which is necessary in protecting the growth of silver particles through aggregation.

In the formation of silver nanoparticles by the chemical reduction method, the particle size and aggregation state of silver nanoparticles are affected by various parameters, such as initial $AgNO_3$ concentrations, reducing agent/$AgNO_3$ molar ratios, and stabilizer concentrations. Besides that, this method also can controlled the morphologies with the strongly during the synthesis because it is very strong depend on the temperature adopted (Reza et al., 2011). Based on this method also, the size of particles will achieve in range 10 to 100 nm.

CHAPTER 3

METHODOLOGY

3.1 MATERIAL AND SOLVENTS

The synthesis of silver nanoparticles was carried out using standard synthetic chemical procedure and commercially available reagents. Glucose and Cetyl trimethylammonium bromide (CTAB) were purchased from Sigma Aldrich with purity 96 % and 99%, respectively. Ascorbic acid with purity 99% is used as a surfactant which is a reagent grade also purchased from Sigma Aldrich. Besides that, silver nitrate ($AgNO_3$) with purity 99.9% in a crystalline form also purchased from Sigma Aldrich is used as a precursor for synthesis of silver nanoparticles. For analysis of sample, ethanol were used with purity 99.5% and also purchased from Sigma Aldrich. The entire chemicals were used as received without purification.

3.2 APPARATUS AND EQUIPMENT

For synthesis of silver nanoparticles, the main apparatus and equipments that have been used were 250 ml two-neck-flask, thermometer, magnetic bar, thermometer stand and hot plate with magnetic stirrer. The other apparatus in preparations of solutions is 600ml beaker, 250 beaker, stopper and 50 ml measuring cylinder. During the centrifugation process, the centrifuge tubes were needed for centrifuge the sample. After that, ultrasonic cleaning also used as an equipments for the preparation on synthesis of silver nanoparticles. For this part, a beaker is needed to cleaning the samples.

In this study, the samples obtained in synthesis process were characterized using UV-Vis adsorption spectroscopy, Field Emission Scanning Electron Microscopy analysis (FESEM) and Energy Dispersive X-ray spectroscopy (EDX). The freeze drying cuvette is used for UV-Vis adsorption and dropper for drop the sample on study for analysis of FESEM and EDX.